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# Relative Diffusivities from Breakthrough Curves through Exchange Adsorption

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## Abstract

The relationship between chromatographic peaks and breakthrough curves manifests itself through the similarity of the "variance" and the volume of gas adsorbed.

A new technique with some outstanding features, the exchange adsorption between two similar gases, is introduced. With this technique the relative diffusivities of ethane and ethylene were measured at high gas flow rates. The large difference found between relative diffusivities could explain why adsorptive separation, if technically feasible, is superior to distillation.

## INTRODUCTION

Chromatographic and breakthrough curves are closely interrelated. One may quote the analytical importance of the former and the industrial significance of the latter. In both cases the physical processes involved are the same, namely adsorption and diffusion, except that the chromatographic peak displays the rules of the distribution of an "impulse-function" concentration input, whereas the breakthrough curve is that of a "step-function" input; therefore, in both cases for the same system, the same mathematical model is applicable.

## EXCHANGE ADSORPTION

Assume two gases having similar physical properties (that is, adsorptivity and diffusivity), such as ethane and ethylene. Let an adsorbent column be saturated with one of the component, say ethylene. After complete saturation the other component, ethane, is introduced, either in the form of an impulse-function or of a step-function, resulting in either a chromatography peak or a breakthrough curve. The process is reversible; i.e., one may start with ethane followed by ethylene. In terms of chromatography, this means that the adsorbent column is first saturated with a gas which adsorbs almost as well as the adsorbate proper, then the sample is introduced while the saturating gas is used as carrier. The advantages of this technique can be summarized as follows.

*Linearity (Ideality) of the Mass Transfer Mechanism.* In many cases the relative adsorbability of several binary mixtures is linear for the entire range of the isotherm. This is particularly valid when physical adsorption is involved, as has been shown by Lewis et al. (*9*). Their equation, in terms of ethane and ethylene, is

$$\frac{N_E}{N_E'} + \frac{N_Y}{N_Y'} = 1 \tag{1}$$

where $N_E$ and $N_Y$ are the amounts of ethane and ethylene adsorbed from the mixture, and $N_E'$ and $N_Y'$ are the adsorption capacities for the pure components.

*Reversibility.* From the linearity it follows that the output distribution curves are similar in shape, regardless of the sequence in which the exchange adsorption is performed. Note, however, that if the lesser adsorbing component, say ethylene, is used for saturation, combined with the better adsorbing component, say ethane, as adsorbate, the resulting output distribution curve will be sharper than in the reverse case.

The significance of this reversibility manifests itself in two ways. First, the uncommon flat curve takes longer time to develop, and consequently the data conveyed are more accurate and reliable. Second, the relative diffusivities from the flat and sharp curves can be extracted, thus serving as important design data for industrial gas separation technology (*13*, *14*).

*Minimum Change of Gas Flow Rate during Adsorption.* Whereas this change in common adsorption is equal to the rate of adsorption, i.e., to the rate of adsorbate disappearing from the gas phase, in exchange adsorption this rate is reduced to the difference in adsorbability of the two components involved and is often negligible for the entire range of the isotherm. An equation derived for the change of gas velocity for the case when Eq. (1) is valid has been derived (*11*, *12*):

$$v = \frac{v_0}{a + bC} \tag{2}$$

where the magnitude of the constants $a$ and $b$ depend upon the ratio of $N_E'$ and $N_Y'$.

### In General

In the field of adsorption dynamics, exchange adsorption appears to have the potential to become a powerful tool for extracting scientific information as well as for supplying important design data. Its analytical usefulness may also be considered.

## THEORY

There are several theories available to describe dynamic adsorption (*15*, *16*). As pointed out before, they are not restricted either to the impulse or step input involved. Equations derived from the well-known plate theory (*3*) are practical in routine chromatography. For the breakthrough curves, equations derived from the continuity equation are preferred because (a) of their greater flexibility and (b) they come closer to the physical nature of the mass transfer involved.

For dynamic adsorption in a column, the continuity equation can be written (*1*):

$$\underbrace{-A\varepsilon_b \frac{\partial(\rho v C)}{\partial z}}_{\text{I}} = \underbrace{A\varepsilon_b \frac{\partial(\rho C)}{\partial t}}_{\text{II}} + \underbrace{A\rho_b \frac{\partial w}{\partial t}}_{\text{III}} \tag{3}$$

where $\varepsilon_b$ is the void fraction of the bed, $C$ is the mole fraction of the adsorbate in the gas phase, $A$ is the area of mass transfer, $\rho$ is the density of the gas, $\rho_b$ is the bulk density of the adsorbent, and $w$ is the adsorbent load (weight of adsorbate/weight of adsorbent).

This is the so-called "plug flow" model. Thus Term I represents the concentration change along the column, while Terms II and III represent accumulation in the gas phase and adsorbent phase, respectively. In reality the accumulation in the gas phase is zero, but it is usual to replace it by eddy and longitudinal diffusivity terms.

Assuming constant $\rho$, Eq. (3) can be transformed to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{4}$$

providing the following conditions exist:

(a) Linear adsorption isotherms prevail.

(b) Terms II and III represent diffusion processes and can be combined. In that case Term II is substituted for by longitudinal and eddy diffusivity expressions, while Term III is replaced by gas-phase to solid-phase diffusivity term.

(c) The propagation of the distribution curve along the column is constant.

The resulting overall diffusivity $D$ is now a composite constant of all the diffusivities and is in functional relationship with the process parameters such as pore size, gas velocity, column length, and tube diameter.

In Eq. (4), $x$ is the distance in the direction of mass transfer inside the solid phase, and the concentration change as a function of $x$ cannot be determined experimentally. Interest therefore lies in determining $D$ through mathematical manipulations relying solely on $C$ vs $t$ data. In dealing with the impulse distribution curve this is no problem at all, because the area under the peak renders itself readily for moment analysis. In fact, it is well known that the second moment of Eq. (4), the variance $\sigma^2$, is related to $D$:

$$\sigma^2 = 2Dt \tag{5}$$

In general, first, second, and even higher moments may yield valuable information about the transfer process providing a mathematical model for the process is known or presumed (*7*, *8*). In general, breakthrough curves are more consistent and accurate than peaks, but they do not yield to moment analyses because the necessary limits on the integral cannot be imposed. Complementary peaks are often used as breakthrough curves in order to determine system constants, as was done by Schneider and Smith (*10*). Many investigators have gotten around this problem by transforming Eq. (4) into a cylindrical or spherical coordinate system by replacing $x$ by $r$, and hence defining the value of the distance of diffusion in the solid by the radius of the cylindrically (or spherically) shaped adsorbent pellets. This transformation, however, is not always warranted, partly because of the irregularity of the shape and size of the adsorbent pellets, but mostly because of the bidisperse, often multidisperse character of most of the granular adsorbents (*5*, *6*). Clearly, preference should be given in that relation to the cartesian coordinate system.

For breakthrough curves, a solution of Eq. (4) for the volume adsorbed is (*2*, *4*):

$$V = -2\sqrt{\frac{Dt}{\pi}} \tag{6}$$

The validity of Eq. (6) can easily be verified through experimental data because a plot of $V^2$ vs $t$ must yield a straight line with a slope of $(4D/\pi)$. (Note the similarity of Eqs. 5 and 6.)

## EXPERIMENTAL

Exchange adsorption breakthrough curves of ethane and ethylene were measured on activated carbon.

Four variables affecting the shape of the transient curves have been measured and reported elsewhere (*11*): the effect of the gas flow rate, the effect of the particle size of the adsorbent, the effect of the diameter of the test column, and the effect of the length of the test column. All experiments have been carried out in pairs; that is, after an ethane-ethylene exchange transient had been measured, an ethylene-ethane transient was also obtained at the same flow rate.

In this paper, only the overall diffusivities are examined as a function of gas flow rate, and overall diffusivities are computed from reported data (*11*) through Eq. (6).

A schematic drawing of the apparatus is shown in Fig. 1. The analysis was performed with a thermal conductivity cell using the technique of frontal chromatography.

The accuracy of the gas flow rate was ±0.1 %, the temperature control of the thermal conductivity cell was ±0.01 °C, and a pressure control of ±0.2 Torr was achieved. Constant pressure was maintained by means of a Cartesian Manostat. All experiments were conducted at 25.00 °C and 760.0 Torr.

Although the apparatus was designed with the objectives described above, it could essentially be made suitable for various types of transient measurement with little or no change in design. It was able to handle various types of binary gas mixtures over practically any concentration range and at pressures and temperature somewhat higher or lower than those given above.

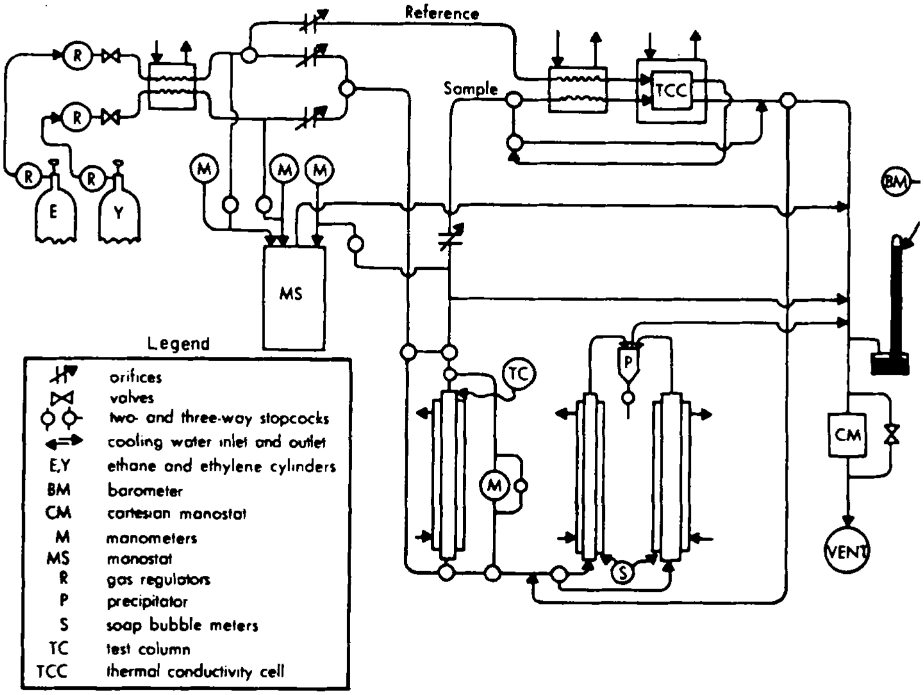

FIG. 1. Schematic diagram of the apparatus for exchange adsorption transient measurements.

## Electronics

The electronic instruments consisted of a Gow-Mac JDC Model 470 Micro Cell, along with a Gow-Mac Voltage Regulated Power Supply Control, Model 40–05 D, and a Model SR Sargent Recorder.

## Gases

Gases were of C.P. grade with a minimum purity of 99.0 and 99.5% for ethane and ethylene, respectively.

## Adsorbent

Pittsburgh BPL activated carbon at mesh size 16/18 US Sieve Series was used as the adsorbent.

### The Column

A glass tube of 3 ft in effective length and 14.5 mm i.d. with an adsorptive capacity of 49.35 and 43.24 $cm^3$ of ethane and ethylene, respectively, at STP per $cm^3$ of packing was used. This amounts to 0.47 $g/cm^3$ bulk density in the column.

## DATA AND RESULTS

### Processing the Data

Data for the ethane–ethylene and ethylene–ethane exchange adsorption were produced at seven different gas velocities in the form of continuous recorder output curves. The abscissa of the curve was time and the ordinata was concentration. From each curve 50 data points were taken at equal concentration intervals and read into a computer wherein, after appropriate instrument and velocity correction, $V$ vs $t$ data were processed through the equation

$$V = \sum_{i=0}^{50} v \left[ 1 - \frac{C_{i+1} + C_i}{2} \right] \Delta t \tag{7}$$

where $C_i$ is the true point concentration in the gas phase and $v$ is the point gas velocity computed by Eq. (2).

### Similarity of the Transfer Mechanism

From the $V$ vs $t$ data as computed above, $V$ vs $t$ curves were drawn on a reduced scale by a Calcomp plotter. Note that reduced $V$ is equivalent to the relative saturation. The Calcomp output resulted in practically identical curves throughout all runs (*11*). Only the ethane–ethylene runs showed some scattering. From this it has been concluded that a similar transfer mechanism (that is, the same differential equation) is valid for each case.

### Choice of Transfer Mechanism

Another plot of $V$ vs $t^{1/2}$ (again on a reduced scale) revealed a straight line portion between about 0.3 and 0.8 fractions of $V$; therefore, Eq. (6) is considered valid for this section.

Figure 2 shows a typical $V$ vs $t$ and a typical $V$ vs $t^{1/2}$ plot on a reduced scale.

### Overall Diffusivities

Overall diffusivities computed from the straight line portion of the $V$ vs

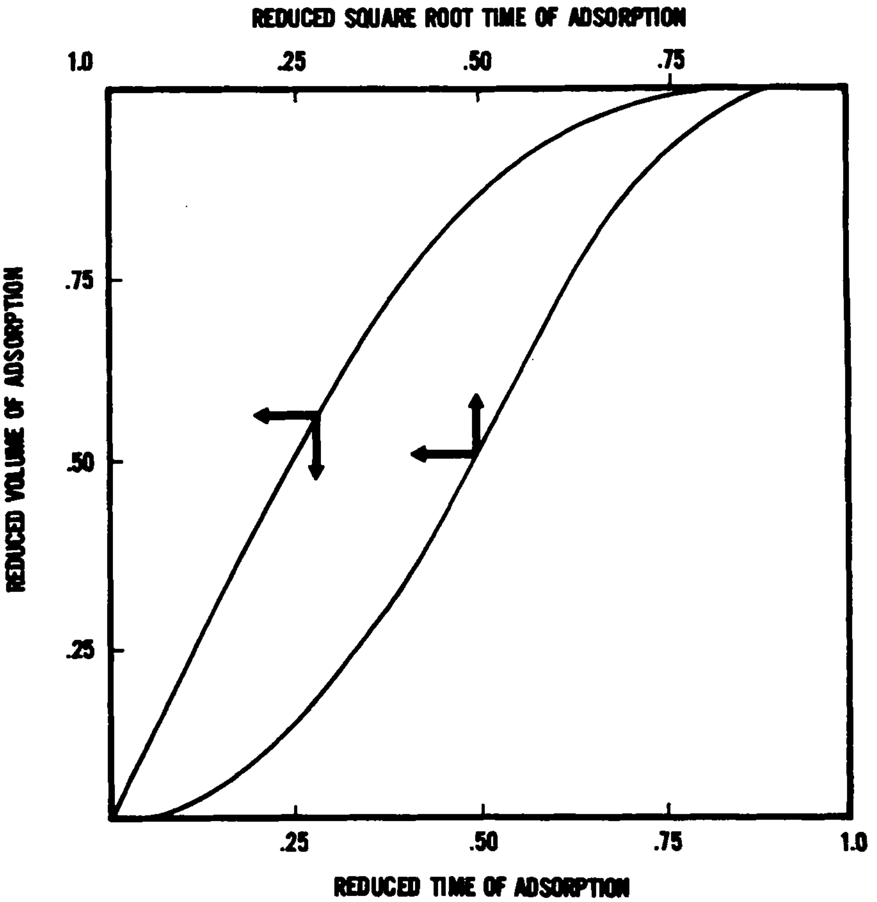

FIG. 2. Plot of reduced volume of adsorption vs reduced time and reduced square root of time of adsorption for a typical run.

TABLE 1

Overall Diffusivities $D$ for Ethane–Ethylene and Ethylene–Ethane Exchange Adsorptions as a Function of Gas Velocity

| Velocity (cm/sec) | $D$ (cm$^2$/sec), ethane–ethylene | $D$ (cm$^2$/sec), ethylene–ethane |
|---|---|---|
| 1.91 | 9.98 | 0.316 |
| 3.05 | 13.94 | 0.479 |
| 5.29 | 18.77 | 0.797 |
| 8.31 | 21.08 | 1.244 |
| 11.81 | 24.86 | 1.586 |
| 16.17 | 31.86 | 2.056 |
| 20.83 | 37.13 | 2.676 |

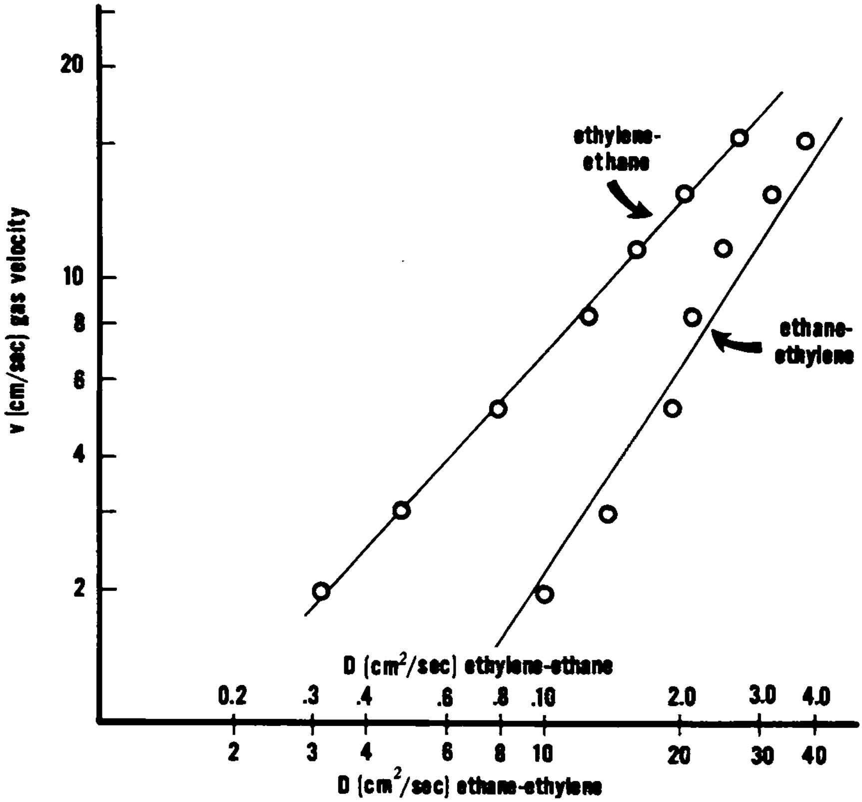

FIG. 3. Overall diffusivities, $D$, for ethane-ethylene and ethylene-ethane exchange adsorption as a function of linear gas velocity.

$t$ plots through Eq. (4) are shown in Table 1. A plot of $v_0$ vs $D$ on a log-log scale is shown in Fig. 3.

### Correlation of Overall Diffusivities

From the slopes and intercepts of the straight line in Fig. 3, linear gas velocities were correlated with overall diffusivities for the ethane–ethylene exchange adsorption:

$$v_0 = (0.055)D^{1.60} \tag{8}$$

and that for the ethylene–ethane exchange adsorption:

$$v_0 = (6.88)D^{1.11} \tag{9}$$

## CONCLUSION

1. From the similarity of the $V$ vs $t$ plots of the breakthrough curves, it has been concluded that one equation can be applied for both ethane–ethylene and ethylene–ethane exchange adsorption as exposed to a variation of gas velocity. This is also true for other parameters, such as particle size of the adsorbent and the diameter and length of the adsorbent column. The ratio of similarity manifests itself only in the magnitude of the transfer constants.
2. Equations (4) through (6) were applied to that part of the breakthrough curve where the $V$ vs $t$ plot displayed a straight line. Although there is little doubt about the validity of Eq. (4), it is obvious that the same mechanism cannot be applied to the entire range of the saturation curve. This is to be expected since activated carbon has a rather complex structure consisting of various sorts of channels which probably obey different transfer mechanism rules and pores of varying diameter with different rates of pore diffusivity. It is probably in the pore structure of the adsorbents that the dynamics deviate from equilibrium predictions.
3. The overall diffusivities $D$, as presented here, incorporate other transfer constants as well, such as constants for the gas phase diffusivities and for the linearity of the adsorption isotherm. It is plausible that the gas phase contributions are the same for one pair of runs and that the solid phase diffusivities remain constant throughout in that they are not in a functional relationship with the process parameters. The difference in the magnitude of the $D$'s would then come only from the difference of the solid phase contributors as the two components, ethane and ethylene, are

interchanged. Anticipating difficulties at this point, no further attempt has been made to break $D$ down to gas- and solid-phase contributors. This will require rather careful study.

4. The most significance of our findings as considered here is the order of magnitude difference between the overall diffusivities of ethane–ethylene and ethylene–ethane runs. This is in contradiction to many of the existing theories (e.g., reciprocity), while on the other hand it is in perfect agreement with practical applications, notably gas separation on moving adsorbent bed (*13*). For gas separation, with few exceptions, this process proves itself superior to distillation (*14*).

5. The analytical application of the exchange adsorption technique is challenging.

## SYMBOLS

| | |
|---|---|
| $A$ | area of mass transfer |
| $C$ | concentration in the gas phase |
| $D$ | overall diffusion constant cm$^2$/sec |
| $N$ | volume of gas adsorbed |
| $N'$ | volume of gas adsorbed at saturation |
| $t$ | time |
| $V$ | volume of gas adsorbed by unit volume of adsorbent bed |
| $v$ | gas velocity, cm/sec |
| $w$ | adsorbent load (weight of adsorbent/weight of adsorbate) |
| $x$ | distance in the direction of diffusion |
| $z$ | distance along the bed |
| $\varepsilon_b$ | void fraction of the adsorbent bed |
| $\rho$ | gas density |
| $\rho_b$ | density of the adsorbent bed |
| $\sigma^2$ | the variance |

### Subscripts

| | |
|---|---|
| 0 | initial value |
| $E$ | ethane |
| $Y$ | ethylene |

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